Notes

Miscibility of Poly(vinyl chloride) with Copolyacrylates

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Received December 1, 1988;
Revised Manuscript Received February 9, 1989

Introduction

A wide range of polyacrylates and polymethacrylates are known to be miscible with poly(vinyl chloride) (PVC).[1-5] It is found that poly(methyl acrylate) (PMA) and polyacrylates with long side chains, such as poly(hexyl acrylate) (PHA), are immiscible with PVC, but polyacrylates with intermediate length side chains, such as poly(pentyl acrylate) (PPeA), poly(butyl acrylate) (PBA), poly(propyl acrylate) (PPrA), and possibly poly(ethyl acrylate) (PEA), are miscible. These miscible pairs show lower critical behavior. The heats of mixing of oligomeric analogues are consistent with the miscibility of the respective polymers.

The phenomenon described above is very similar to the "window of miscibility" observed for copolymers, which has often been attributed to the effect of cross terms, unfavorable interactions between units on the same copolymer which can enhance miscibility.[6-8] In the case of these PVC mixtures, miscibility has also been ascribed to the effect of specific interactions which can cause miscibility in situations where the normal dispersive forces between polymers are small.[9]

The phase separation on heating of polymer mixtures has often been explained by free volume changes causing extra unfavorable contributions to the free energy. In a similar mixture, chlorinated polyethylene with vinyl acetate copolymers, however, it was shown by FTIR that phase separation coincides with the dissociation of hydrogen bonding between the polymers.[10] In PVC/polyacrylate blends, the heat of mixing of low molecular weight analogues was found to be strongly temperature dependent, suggesting that similar effects are also important in these blends.[11]

In this paper, we describe the miscibility of copolyacrylates with PVC, which we hope will elucidate those factors that are important for the miscibility of this type of blend.

Experimental Section

Materials. Acrylate monomers and some of the polymers, PVC and PBA, were obtained commercially (Aldrich Chemical Co.). Other homopolymers were prepared by emulsion polymerization as described elsewhere.[11] Propyl acrylate and pentyl acrylate were prepared from methyl acrylate by transesterification as described elsewhere.[11] The copolymers were prepared by solution polymerization.

A mixture of the monomers (20 parts by weight; washed with NaOH and twice with distilled water, dried over sodium sulfate, and distilled as previously described[11]), acetone (100 parts, distilled), and 2-propanol (0.002 part, used as supplied) was added to a flask and stirred while nitrogen was passed through it for 30 min. The mixture was heated to reflux (56 °C) and azobis(isobutyronitrile) (0.03 part, recrystallized from methanol) predissolved in a little of the acetone was added. The reaction was allowed to continue for 14 h. The mixture was then cooled and precipitated into 3 times its volume of distilled water, reprecipitated from butanone into water, and dried in a vacuum oven at 50 °C for several weeks until no further weight loss was found. The yield ranged from 80% to 95%.

In one case, we prepared a copolymer to low conversion in order to examine what effect variation in polymer microstructure would have on the properties. This was intended to produce a 40:60 PEA/PHA mixture and was prepared from 12.85 g of ethyl acrylate and 37.15 g of hexyl acrylate as above. The reaction was run for approximately 15 min, and the yield was 8.7%.

The polymers were characterized by gel permeation chromatography relative to polystyrene standards and by elemental analysis or NMR. The properties of the polymers are shown in Table I.

Table I
Properties of Polymers[a]

polymer	M_n	M_w	composition
PVC	74 000	170 000	
PPrA	130 000	340 000	
PBA	123 000	383 000	
PPeA	180 000	415 000	
50PBA/50PMA	143 000	314 000	44.6PBA/55.4PMA(n)
50PBA/50PEA	148 000	326 000	43.5PBA/56.5PEA(n)
50PBA/50PHA	123 000	295 000	47.8PBA/52.2PHA(e)
25PBA/75PMA	114 000	286 000	23.7PBA/76.3PMA(n)
25PBA/75PEA	130 000	313 000	22.9PBA/77.1PEA(n)
25PBA/75PHA	109 000	295 000	24.5PBA/75.5PHA(e)
49PPrA/51PPeA	159 000	365 000	48.1PPrA/51.9PPeA(e)
27PMA/73PHA	127 000	305 000	9.7PMA/70.3PHA(n)
55PBA/45PEA	130 000	285 000	52.8PBA/47.2PEA(n)
40PEA/60PHA	172 000	378 000	41.7PEA/58.3PHA(e)
40PEA/60PHA(L)	97 000	208 000	43.2PEA/56.8PHA(e)

[a] (L) = low conversion, (e) = elemental analysis, (n) = NMR.

The blends of all the above polyacrylates with PVC were prepared by dissolving a total of 1 g of the two components in butan-2-one (20 cm^3) with stirring at 65 °C. The solution was purified by centrifugation and poured into a 5-cm petri dish. The solvent was allowed to evaporate with the dish partially covered and the product dried in a vacuum oven until no further weight loss was observed. All the films were clear except for 25PBA/75PMA and 25PBA/75PHA.

The miscibilities of those blends, which were clear, were confirmed by differential thermal analysis, dynamic mechanical analysis, and, in some cases, electron microscopy. This has been described in detail previously for the homopolymers.[11] The results for the copolymers are not presented here but can be obtained.[12]

Cloud-Point Determination by Light-Scattering Turbidimetry. Phase boundaries were determined by measuring light scattered from the samples using a specially designed light-scattering turbidimeter. The films of the polymer blends were supported in a sample holder located in a thermostatically controlled aluminum block. Light from a tungsten lamp was focused onto the sample, and the light scattered at 45 °C was measured by a photodiode. The temperature of the block could be altered at a controlled rate, and a plot of scattered light against temperature was obtained. The results were corrected for changes in sensitivity of the diode with temperature. Abrupt increases in scattered light were considered as evidence of a cloud point. The samples could also be held at a preset temperature, and the increase in scattering could be observed as a function of time. The temperature at which a gradual increase in scattering occurred could be obtained, and this gives a much more reliable measure of the cloud point. The cloud points range from 50 to 200 °C above the blend T_g's. At the lower end of this range, kinetic effects are expected to be more important.

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0024-9297/89/2222-3799$01.50/0

Table II
Variations of Cloud Points of PVC Blends over the Composition Range

2nd component	cloud pt (°C) 2nd component compositions					
	15	25	40	50	60	75
PPrA	164	154	137	129	132	163
PBA	152	143	131	125	131	146
PPeA	130	121	109	106	111	129
50PBA/50PMA	149	144	139	137	142	152
50PBA/50PEA	148	141	134	132	134	148
50PBA/50PHA	117	112	107	105	105	112
25PBA/75PEA	142	137	131	130	134	148
49PPrA/51PPeA	147	137	128	124	126	143
27PMA/73PHA	145	130	118	115	120	149
55PBA/45PEA	155	145	136	132	138	157
40PEA/60PHA	148	137	128	125	128	141
40PEA/60PHA(L)	142	134	126	124	126	134

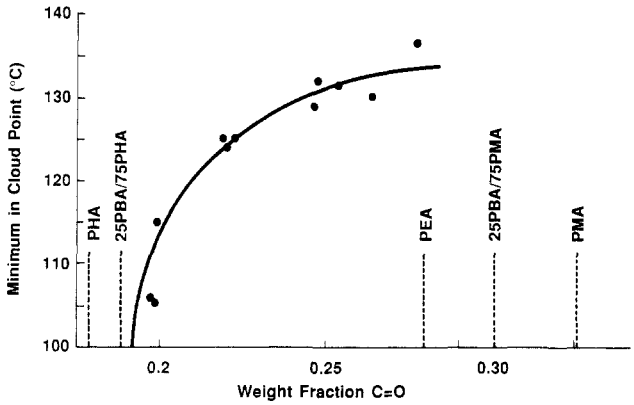

Figure 1. Plot of the minimum in the cloud-point curve for PVC/polyacrylate blends plotted against the weight fraction of C=O groups in the polyacrylate or copolyacrylate. Also shown are several immiscible compositions.

Results and Discussion

The cloud point data for the various blends are shown in Table II.

All of the miscible pairs show minima in the cloud-point data between 100 and 140 °C. It is also apparent that the sample prepared to low conversion gives essentially the same minimum in the cloud-point curve as the similar composition sample taken to high conversion, showing that the higher compositional variation does not affect the results.

Figure 1 shows a plot of the mimimum in the cloud-point curve against the weight fraction of C=O groups in the various polyacrylates, used as an arbitrary parameter depending on the fraction of polar groups in the polymer. Also shown are those compositions that give two-phase blends. It is apparent that the cloud point is simply a function of the weight fraction of C=O groups. For example, PBA, a PPrA/PPeA copolymer, and a PEA/PHA copolymer all contain a 0.22 weight fraction of C=O and have similar cloud points even though PEA and PHA individually form two-phase mixtures.

PEA is known to form two-phase mixtures when solvent cast with PVC but to form one-phase mixtures when prepared by the in situ polymerization of VCM with PEA.[4] PMA always produces two-phase mixtures. It is possible that the casting solvent is the cause of the two-phase mixtures in some cases, since phase separation in polymer/polymer/solvent systems is a common phenomena. It is unlikely that the cloud point is anything other than a smooth function of C=O content.

The cloud points do not appear to be much affected by molecular weights in the range studied. This would confirm that the cloud points are largely determined by the interactions, the temperature dependence of the interactions, and possibly free volume effects.

As the origin of the miscibility of these systems is concerned, this could be inferred to come from specific favorable interactions with PVC or from unfavorable cross terms between ester groups and hydrocarbon groups in the polyacrylates. One could equally have said that the miscibility of a PEA/PHA copolymer could be attributed to an unfavorable interaction between ethyl acrylate and hexyl acrylate units. This is not a particularly useful statement, however, since PBA shows identical miscibility. In theories that calculate cross terms, the division of a polymer into parts is essentially arbitrary. Whereas some divisions are mathematically equivalent, different divisions may lead you to believe that different effects cause miscibility. If one were to state that a favorable interaction of the type demonstrated in ref 10 was the origin of miscibility, then one would claim that miscibility occurred over a range of compositions where the normal unfavorable interactions nearly balanced out, that is, where the two polymers have similar solubility parameters. Whereas these appear to be very different descriptions of the system, it may be that in some cases such descriptions are not mutually exclusive when related to the individual group interactions.

Registry No. PVC, 9002-86-2; PPrA, 24979-82-6; PBA, 9003-49-0; PPeA, 37017-37-1; (PBA)(PMA) (copolymer), 25852-39-5; (PBA)(PEA) (copolymer), 26353-42-4; (PBA)(PHH) (copolymer), 26353-42-4; (PBA)(PPeA) (copolymer), 120411-53-2; (PMA)(PHA) (copolymer), 120411-55-4; (PEA)(PHA) (copolymer), 120411-56-5.

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Microstructures of Commerically Available Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)s

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Received October 13, 1988;
Revised Manuscript Received December 27, 1988

The bacterially synthesized polyesters, poly(3-hydroxybutyrate) (PHB) and its copolyester with 3-hydroxyvalerate (PHB–HV), are optically active and biodegradable polymers. These polymers are very interesting materials because of their unique properties.[1-3]

0024-9297/89/2222-3800$01.50/0